CORRELATION BETWEEN THERMALLY STIMULATED LUMINESCENCE AND CERAMIC PROPERTIES OF BERYLLIUM OXIDE (A REVIEW)

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Thermally stimulated luminescence (TSL) of BeO powders and ceramic samples of density $2.10 – 2.93$ g/cm^3 made of the same batch of powder is investigated. It is established that with increasing density of BeO samples (and, accordingly, increasing mean size of microcrystals), as well as with increasing vacuum in a cryostat chamber, the positions, number, and intensity of low- and high-temperature TSL peaks of adsorption and non-adsorption origin are modified. It is assumed that impurity and adsorption centers of volume and surface origin, as well as internal lattice defects, are responsible for the formation of TSL centers in BeO powders.

Beryllium oxide is of practical interest as a working body for tissue-equivalent thermoluminescent, exoelectron-emitting, and EPR (electron paramagnetic resonance) dosimeters [1 – 4].

To increase the reliability of registered information in using beryllium ceramics as a detector in ionizing radiation dosimeters, it is essential to know the relationship between thermally stimulated luminescence (TSL) and the average size of microcrystals, the density of ceramics, and the value of the vacuum in the cryostat chamber in which radiation and heating of samples is carried out.

The existence of TSL peaks with maxima at temperatures of 96, 143, 187, 233, 450, and 600 K in BeO was reported earlier [5]. The activation energy values for high-temperature TSL peaks in BeO were calculated in [6, 7], and an energy diagram of peak traps was plotted. The authors of [3] noted variations in the shape, intensity, and maximum temperature of the TSL peak in various BeO samples. The authors in [1] studied the effect of impurity ions (Li, Na, Si, Ge, B, and Al) on thermoluminescence in BeO.

Many authors believe there is a correlation between the formation of certain TSL peaks and the structural defects of the lattice. We are of the same opinion.

Samples of BeO powders for experiments were obtained by heat treatment of beryllium hydroxide β-Be(OH)$_2$ at temperatures of 770 and 1370 K. Samples were obtained by semidry compression of BeO power with an organic binder additive. After compression, the molded disks were subjected to burning-out of the binder at the maximum temperature of 1370 K (the "binder burnout" operation). The sample

density at that time was $2.10 – 2.20$ g/cm^3. To obtain densely sintered ceramics, samples after burning-out of the binder were heat-treated at the maximum temperature of 2220 K in a forevacuum. All samples were prepared from the same batch of initial BeO powder.

TSL spectra of BeO powders and ceramics were analyzed on an equipment consisting of a URS-55A x-ray unit and a vacuum cryostat chamber allowing for radiation, heating, and cooling of samples within a temperature range of $77 – 800$ K and at a maximum vacuum level up to 133.2×10^{-4} Pa. TSL spectra were registered using an optical monochromator to identify the spectral composition of various TSL peaks, and also on a FÉU-106 electron multiplier in the integral mode. The radiation conditions and the heating rate of samples were equal in all experiments.

TSL peaks virtually cannot be registered in BeO powder obtained after decomposition of beryllium hydroxide at 770 K because of the extremely small mean size of microcrystals. Heat treatment of BeO powder at 1370 K leads to emergence of registrable TSL depending on the temperature of preliminary radiation. Radiation of powder at 77 K yields two weak low-temperature peaks (88 and 143 K) and also two high-temperature peaks: a weak one at 353 K and a more intense one at 593 K (Fig. 1, curve *1*).

After burning-out of the binder, ceramic articles typically exhibit a minimal number of TSL peaks of relatively low intensity and a greater half width than ceramics produced by sintering at 2220 K. The average size of BeO microcrystals has a decisive effect on the type of TSL spectra. Ceramic samples after burning-out of the binder have a low density $(2.10 – 2.20$ g/cm^3) and high porosity and contain an increased quantity of impurities introduced via the initial BeO powder and remaining after pyrolysis of the organic binder.

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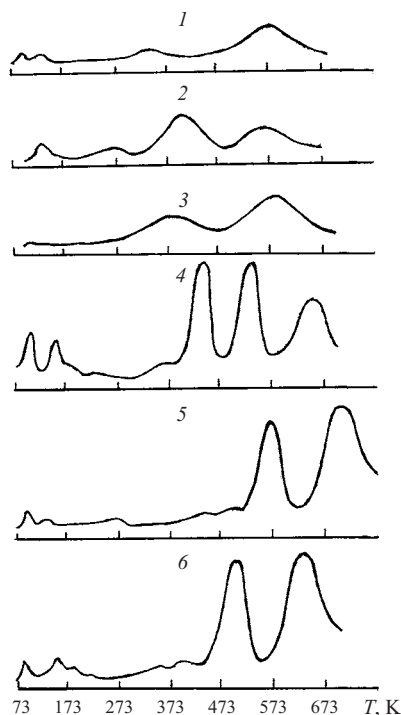
Fig. 1. TSL spectra of powders and beryllium ceramics of different density after x-ray excitation at a temperature of 77 K: *1*) BeO powder after additional heat treatment of initial β-Be(OH)$_2$ at 1370 K, vacuum 133.2×10^{-4} Pa; *2* and *3*) beryllium ceramics (after the binder is burned out) of density $2.10 - 2.20$ g/cm^3, vacuum 57.3 and 133.2×10^{-4} Pa, respectively; *4*, *5*, and *6*) beryllium ceramics of density 2.86, 2.90, and 2.93 g/cm^3, respectively, vacuum in all cases 133.2×10^{-4} Pa.

TABLE 1

$V = 39.9$ Pa, $T_{exc} = 273$ K		$V = 29.3$ Pa, $T_{exc} = 77$ K		$V = 133.2 \times 10^{-4}$ Pa, $T_{exc} = 77$ K		$V = 37.3$ Pa, $T_{exc} = 243$ K	
T_m, K	E_a, eV	T_m, K	E_a, eV	T_m, K	E_a, eV	T_m, K	E_a, eV
353	0.90	93	0.15	98	0.17	–	–
438	1.70	158	0.50	153	0.80	–	–
533	2.50	173	0.60	448	1.90	–	–
673	3.60	423	1.40	–	–	433	1.60
–	–	543	1.90	533	2.90	538	2.30
–	–	670	3.50	673	3.80	683	3.90

These samples typically have a smaller mean size of microcrystals $(1.5 - 3.0 \,\mu\text{m})$ than samples of density $2.86 - 2.93$ g/cm^3, in which the average size of microcrystals is in the limits of $20 - 50 \,\mu\text{m}$. Note that the theoretical density of BeO is 3.01 g/cm^3.

The character of TSL spectra is significantly affected by the value of the vacuum in the chamber. The TSL spectra of ceramics discs after burning-out of the binder in a vacuum of 57.3 Pa and x-ray radiation at 77 K exhibit peaks at 128, 293, 423, and 573 K (Fig. 1, curve *2*). Repeated heating of the samples in the same vacuum at 750 K and x-ray radiation at 77 K result in disappearance of the intense low-temperature peak at 128 K and the weak peak at 293 K. The intensity of the remaining two peaks is redistributed and their positions on the temperature scale change. The peak with a maximum at 423 K becomes less intense and is shifted toward lower temperatures (to 393 K), whereas the high temperature peak at 573 K is shifted toward higher temperatures, i.e., to 598 K (Fig. 1, curve *3*). Subsequent heating and radiation of the same samples at 77 K in a vacuum of 133.2×10^{-4} Pa result in shifting of the TCL peaks toward the high-temperature range (433 and 613 K). As a consequence, the TCL spectra of ceramics after burnout of the binder exhibit two high-tem-

perature TSL peaks in the temperature intervals of $393 - 433$ and $573 - 613$ K.

A further sintering of samples after burnout of the binder to a density of 2.86 g/cm^3 increases the mean size of BeO microcrystals (to about 25 μm) and is accompanied by a modification of TSL spectra (the number of peaks, the maximum temperatures, increasing intensity, and decreasing half width of the peaks). Radiation of these samples at different temperatures in forevacuum leads to the emergence of weak and intense peaks of adsorption origin in a temperature interval of $93 - 378$ K and intense peaks in an interval of $423 - 673$ K. After the level of vacuum in the chamber is brought down to 133.2×10^{-4} Pa and samples are heated at 750 K, the weak TSL peaks (263, 313, and 378 K) disappear, and the three most intense peaks (448, 533, and 673 K) remain in the spectrum (Fig. 1, curve *4*). A multiple heating to 750 K and cooling of samples in the same vacuum is accompanied by an insignificant decrease in the intensity of the peak at 448 K. A decrease of vacuum in the chamber again results in emergence of weak peaks of sorption origin and three high-temperature peaks with maxima at 538, 568, and 663 K.

In accordance with the Balarin and Zetshce method [8], the activation energy values of the main TSL peaks in beryllium ceramic samples sintered to a density of 2.86 g/cm^3 were calculated using a computer. The temperatures of the maxima T_m and activation energy E_a of the main TSL peaks of such ceramics depending on the value of the vacuum V and the temperature T_{exc} at which the samples were excited are given in Table 1.

Sintering of samples to a density of 2.90 g/cm^3 modifies the TSL spectra. After the samples are radiated in vacuum of 29.3 Pa, the spectra exhibit low-temperature (148, 168, 273, 330 K) and high-temperature (478 and 593 K) peaks. A decrease in vacuum to 133.2×10^{-4} Pa, heating at 750 K, and radiation at 77 K are accompanied by emergence of low-temperature peaks (83, 93, 113, and 133 K) and two intense ones (548 and 673 K) in the TSL spectra (Fig. 1, curve *5*). Multiple heating to 750 K and cooling of samples in the same vacuum lead to a substantial decrease in the peaks of sorption origin (83, 93, 113, and 133 K) and finally to their complete disappearance.

Compared to samples of density 2.86 and 2.90 g/cm³, sintering of the same BeO powder to a density of 2.93 g/cm³ is accompanied by a further increase in the mean size of microcrystals (45 – 50 μm) and a decrease in the overall porosity. When a ceramic sample of density 2.93 g/cm³ is x-radiated in a vacuum of 50.6 Pa at room temperature, its TSL spectrum exhibits three peaks: 373, 478, and 603 K. Heating of the same sample in a vacuum of 133.2×10^{-4} Pa and its radiation at 77 K lead to the appearance of numerous maxima at 83, 153, 173, 358, 388, and 433 K and the two brightest maxima at 473 and 633 K. Repeated radiation of the same sample under the same conditions results in the disappearance of the weak peak at 433 K. The most intense TSL peaks in that case have maxima at 488 and 608 K (Fig. 1, curve *6*). A decrease in the vacuum level to 23.9 Pa and x-ray irradiation at 77 K again increase the intensity of the low-temperature peaks at 83, 153, and 173 and results in the emergence of a peak at 423 K.

The activation energy values for the TSL peaks of beryllium oxide at 348, 473, 633, 807, and 905 K were calculated in [6, 7] and constituted 0.7, 1.0, 1.8, 2.3, and 4.5 eV, respectively. As follows from the data in Table 1, there are substantial discrepancies between the temperature positions of the TSL peak maxima and their activation energies and the results of studies in [6, 7]. These discrepancies are due to several factors, the main of which are the existence of impurities, the mean size of microcrystals, the rate of heating and cooling of samples, and the value of the vacuum under which the measurements are taken.

The authors in [1] attribute the existence of TSL at 453 K to the presence of Li and Na impurities in BeO. A chemical analysis performed by us also identified the presence of Na and Li impurities in beryllium ceramics. The impurities persist in the BeO powder in the course of processing and sintering of ceramics. As a consequence, the high-temperature TSL peak (448 – 488 K), which changes to some extent its position on the temperature scale depending on the excitation conditions, can be related to the effect of uncontrolled Na and Li impurities.

The TSL peaks in the temperature range of 80 – 438 K are probably of sorption origin. X-ray irradiation of BeO can activate structural defects (such as ruptured bonds on the surface) leading to the formation of long-lived adsorption centers.

X-ray irradiation of BeO powders or ceramics heat-treated at high temperatures (1600 – 2000 K) in vacuum or in a reducing atmosphere is accompanied by the formation of an EPR signal (an electron center), in which an electron is localized on an anion vacancy (a F^{-} or F^{+} center). Such an electron later serves as an absorption center for gases and radicals. In addition to an electron center in BeO (after x-ray radiation) cooled in air or in oxygen, in using the EPR method, we registered hole centers connected with an oxygen ion, next to which there is a beryllium vacancy.

According to the data in [9, 10], water molecules adsorbed on BeO from a residual atmosphere in the chamber decompose under UV radiation releasing H_2 and O_2 into the gas phase. In the course of irradiation of BeO, one can observe photosorption of oxygen and hydrogen and photocatalytic oxidation of hydrogen [9 – 11]. In the presence of H_2 and O_2, hydroxyl groups and water molecules are formed on the irradiated surface of BeO. It can be assumed on this basis that complex photocatalytic and photosorption processes take place on the surface of ceramics irradiated with x-rays in a cryostat chamber.

As was earlier reported [12], anomalies were registered in the temperature dependence of heat capacity in the course of BeO cooling in a temperature range of 340 – 77 K under a constant pressure and a constant TCLE. The anomalies $c_p(T)$ and $\alpha(T)$ in BeO are related to phase transformations accompanied by significant static shifts of Be^{2+} ions in the crystal lattice points, which leads to the formation of a certain number of cation vacancies, in which holes are localized under radiation. This can account for the formation of hole centers in BeO in cooling.

The phase transformations are accompanied by a deformation of the BeO crystal lattice. An anomalous modification of the parameters of the crystal lattice of BeO ceramics was detected in cooling within a temperature range of 180 – 343 K [13]. This leads to the emergence of intense pyroelectric fields in the volume of BeO microcrystyals. The electric field in time relaxes on the surface of the microcrystals. The electric charge is compensated by means of the BeO surface adsorbing residual gasses, ions, polar molecules, and radicals in the cryostat chamber. The intensity of a pyroelectric field depends on the mean size of BeO microcrystals. As the size of microcrystals (and, accordingly, the sample density) increases, the intensity and number of TSL peaks of adsorption origin increase as well.

Beryllium oxide is a linear pyroelectric that has negative values of the pyroelectric coefficient within a temperature interval of 4 – 300 K [14, 15]. It is known that monocrystals and large-crystalline samples of BeO possess spontaneous (without ionizing radiation excitation) luminescence and exoelectron emission in cooling and heating [12]. This supports the assumption of intense electric fields arising in the volume and on the surface of BeO microcrystals.

Variations in the time of spin-lattice relaxation t_1 of excited ^9Be nuclei depending on temperature were studied using the nuclear magnetic resonance method [16]. It was found that t_1 in cooling of samples (from 370 to 77 K) significantly depends on the average size of BeO microcrystals. It can be assumed that the increase in t_1 is related to the influence of intense pyroelectric fields arising in the largest BeO crystals. Thus, in ceramics of density 2.89 g/cm³, in which the average crystal size is about 45 μm, t_1 varies in an interval of 295 – 426 sec, whereas in a powdered material with mean crystal size 1.5 – 3.0 μm, it varies from 0.86 to 31.90 sec. Accordingly, the sequence of TSL peaks in BeO powders and ceramics in a temperature range of 83 – 438 K has an absorption nature related to electrostatic sorption of

ions, polar molecules, and radicals and disappears or significantly modifies its intensity upon heating up to 800 K in vacuum of 133.2×10^{-4} Pa.

Of special interest is the TSL peak within a temperature range of $393 - 438$ K. Experiments showed that the position of this peak and its intensity are related not only to the level of vacuum in the chamber and the mean size of the microcrystals, but also to the duration of sample exposure at a temperature of 77 K. High cooling raters ($30 - 60$ K/min) result in increasing temperature of the TSL peak and its intensity. Multiple heating and cooling of samples in vacuum of 133.2×10^{-4} Pa significantly decreases its intensity. Hence it can be assumed that this peak is related to the pyroelectric effect and is determined by electrostatic sorption of ions and radicals from the residual atmosphere in the chamber.

The two high-temperature TSL peaks in the temperature intervals $440 - 478$ and $533 - 679$ K are not of adsorption origin. Heat treatment of powders and ceramics in vacuum at $1800 - 2000$ K increases the intensity and temperatures of non-adsorption TSL peak maxima, which suggests the existence of a relationship between the internal defects (cation and anion vacancies) of the BeO crystal lattice and TSL. It is established that a certain effect on the intensity of these peaks is exercised as well by the level of vacuum in the cryostat chamber. The experiments performed in multiple heating, cooling, and radiation of ceramics of different densities in vacuum of 133.2×10^{-4} Pa using the same dose of x-radiation indicated a high stability of TSL spectra (positions and intensity of the two high-temperature peaks) in samples of density 2.86 g/cm³, which is evidence of the optimum size (about 25 µm) of microcrystals in these samples. Ceramic samples of density 2.93 g/cm³ with a mean microcrystal size about 50 µm exhibit parasitic (spontaneous, without x-ray radiation, occurring both in heating and cooling) TSL signals determined by the effect of intense pyroelectric fields.

The spectral composition of high-temperature TSL peaks of powders and ceramics under x-ray excitation was investigated. It was found that the TSL peak in the temperature range of $440 - 478$ K differs in its spectral composition from the peak at $533 - 679$ K. Its spectral maximum is within a range of $4.0 - 4.2$ eV, whereas the spectral position of the second maximum is within a range of $4.4 - 4.6$ eV.

X-radiation ionizes the residual atmosphere in a cryostat chamber and excites the surface and volume centers in BeO, and at that time, complex photocatalytic processes take place on the surface of ceramics. Decomposition of water and OH groups as a consequence of a photocatalytic reaction leads to the formation of mobile atoms and ions of hydrogen and chemically active anion-radicals of O^-. As a result of letting air into the chamber and radiating samples in low vacuum, photosorption of oxygen and OH groups occurs on the structural defects of BeO. At the same time, the dissociation energy of surface hydroxides and water molecules coordinated on the surface significantly changes. This can account for a

shift in the TSL peaks depending on the level of vacuum in the cryostat chamber.

Thus, thermally stimulated luminescence in BeO powders and ceramic samples of density $2.10 - 2.93$ g/cm³ obtained from the same powder batch was investigated. It was found that with increasing density of samples (and, accordingly, increasing mean size of microcrystals), as well as with increasing vacuum in the cryostat chamber, the positions, number, and intensity of low- and high-temperature TSL peaks of adsorption or nonadsorption origin are modified. Intense pyroelectric fields arising in the volume of large BeO microcrystals acting as adsorption centers for ions, polar molecules, and radicals have a great effect on TSL spectra. X-ray radiation of beryllium ceramics under different levels of vacuum is accompanied by photocatalytic and photosorption processes also affecting TSL spectra.

On this basis it can be assumed that impurity and adsorption centers of surface and volume origin as well as inner lattice defects are responsible for the formation of TSL centers in BeO powders and ceramics of different densities.

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